

[beginning of this sentence illegible] REPRODUCED OR STORED ELECTRONICALLY WITHOUT WRITTEN PERMISSION FROM THE COPYRIGHT HOLDER. UNAUTHORIZED REPRODUCTION MAY RESULT IN FINANCIAL AND OTHER PENALTIES.

[19] State Intellectual Property Office of the People's Republic of China

[51] International Classification⁷: BO1J 23/755, BO1J 23/888

[12] Public Notice of Patent Application

[21] Application number: 99113805.8

[43] Publication date: March 21, 2001

[11] Publication number: CN 1287882A

[22]	Application date:	June 24, 1999
[21]	Application number:	99113805.8
[71]	Applicant:	China Petrochemical Corporation
	Address:	100029 Beijing City Chaoyang District, Huixin Street East No. A6 Shanghai Research Institute of Petrochemical Technology (China Petrochemical Corporation)
	Co-applicant:	An Wei, Guo Ping, Dai Yimin, Chen Xin
[72]	Inventors:	Shanghai Patent Agency
[74]	Patent agent:	Yuan Mingchang, Zheng Cunming

Claims: 2 pages

Description: 6 pages

Accompanying Diagrams: 0 pages

[54] Name of invention: Fluidized-bed catalyst for propylene ammoxidation

[57] Abstract:

This invention relates to a fluidized-bed catalyst for propylene ammoxidation, comprising silicon dioxide as support and a composite of the following formula:

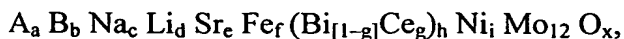
$A_a B_b Na_c Li_d Sr_e Fe_f (Bi_{[1-g]} Ce_g)_h Ni_i Mo_{12} O_x$, wherein A is at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, samarium; B is one element selected from the group consisting of magnesium, zinc, cobalt, manganese, chromium, phosphorus, antimony, boron, tungsten, vanadium or a mixture thereof. The catalyst is able to adjust to high operating pressures and loads, and also exhibits high catalytic activity and a high yield rate of acrylonitrile, making it suitable for industrial use.

[ISSN] 1008-4274

Published by the Intellectual Property Office Publishing House

Claims

1. A fluidized-bed catalyst for propylene ammoxidation, comprising silicon dioxide as support and a composite of the following formula:



where A is at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, samarium;

B is one element selected from the group consisting of magnesium, zinc, cobalt, manganese, chromium, phosphorus, antimony, boron, tungsten, vanadium or a mixture thereof;

a, b, c, d, e, f, and i are ratios of A, B, sodium, lithium, strontium, iron, and nickel, respectively, to 12 molybdenum atoms, g is the ratio of a cerium atom to the sum of a bismuthum and a cerium atom, and h is the ratio between the sum of a bismuthum and a cerium atom to 12 molybdenum atoms; where

a = 0.001 to 0.7;

b = 0.1 to 10;

c = 0.01 to 0.7;

d = 0.01 to 0.7, provided that that a, c and d are 0.1 to 1.5;

e = 0.01 to 4;

f = 0.5 to 4;

g = 0.3 to 0.8;

h = 0.5 to 2;

i = 0.5 to 10;

x = number of oxygen atoms required to satisfy the valence requirement of the other elements present;

the content of silicon dioxide support in the catalyst is in the range of 30-70 percent by weight.

2. A catalyst based on claim 1, wherein a, c, and d are all in the range of 0.2 to 1.0.
3. A catalyst based on claim 1, wherein e, f, and i are in the range of 0.01 to 2.5, 1 to 3 and 2 to 8 respectively.
4. A catalyst based on claim 1, wherein h is in the range of 0.7 to 2.
5. A catalyst based on claim 1, wherein the content of silicon dioxide support in the catalyst is in the range of 40-60 percent by weight.

Description

Fluidized-bed catalyst for propylene ammoxidation

The present invention relates to a fluidized-bed catalyst for propylene ammoxidation, in particular, to an acrylonitrile fluidized-bed catalyst produced by propylene ammoxidation with strontium, cerium and lithium.

Acrylonitrile is an important organic industrial material produced by propylene ammoxidation reactivity. Continuous investigation has been made into obtaining a highly active and selective fluidized-bed catalyst for this purpose, resulting in a series of improvements in catalyst activity. Emphasis has been placed upon collocation of the active components in order to increase activity and selectivity of the catalyst, thereby increasing the single pass yield rate of acrylonitrile as well as the production load.

In acrylonitrile production facilities, we hope the acrylonitrile catalyst can be used under conditions of high propylene load and high reaction pressure, along with achieving a high level of reactivity. This has always been the goal for acrylonitrile manufacturers. High loads and high pressure reactivity can increase both acrylonitrile yields and the reactor's processing capacity. For production facilities of sufficient size, a high load catalyst can decrease catalyst volume and expand reactor capabilities, allowing the manufacturer to adjust production yields based on market demands. High pressure catalysts can fulfill the increasing demands for environmental protection, as the absorption column can utilize the pressure at the top of the column to discharge directly into the furnace for combustion, thereby decreasing pollution associated with the release of unprocessed waste directly into the air.

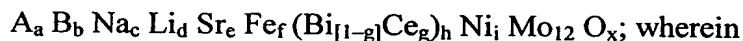
High load and high pressure mean an increase in the density of the propylene, ammonia and oxygen in atmosphere of the reaction, requiring that the catalyst be able to process even more of the reactant per unit time. Therefore, the nature of the catalyst's reactivity under high load and high pressure conditions is reflected in the level of its activity and selectivity, placing a larger demand on the overall performance of the catalyst itself.

US patent 4,228,098 introduced a process of producing acrylonitrile from the ammoxidation reaction of propylene using a catalyst with molybdenum, bismuthum, iron, calcium and phosphorus as its main active components. It does not use chromium. It is important that bismuthum and iron are maintained in fixed proportion to each other in order for the catalyst to exhibit a heightened overall performance. The test was done under the following conditions: a catalyst in a fluidized bed reactor with a propylene load at 0.050 WWH and pressure at 0.05 MPa produced its highest single pass yield of acrylonitrile at 80.9%. Test data for catalysts under high propylene load rates and high pressures were not published. Nevertheless, it can be seen from the published data that when other reactive conditions remain unchanged, acrylonitrile single pass yields produced under 0.05 MPa of pressure are almost 5% lower than those produced under normal pressures. The patent suffers from the following shortcomings: 1) A lack of data made under conditions of high propylene load rates and high reactivity pressure. This means that the production capacity of such facilities is lower; 2) Single pass yield rates of acrylonitrile are not very high either.

Japanese patents JP7289901 and JP7328441 introduce, respectively, Mo-Bi-Ce-Fe-Co and Mo-Bi-Ce-Fe-Ni fluidized bed catalysts for acrylonitrile. These two patents regulate the proportion of bismuthum and cerium to each other in the composition of the catalyst, believing that this kind of ammoxidation catalyst not only produces higher yields of acrylonitrile, but with extended reaction times can effectively prevent yield attrition. The test conditions were 1000 to 2000 g of catalyst in a fluidized bed reactor, with pressure at 0.5 kg/cm², a temperature of 430 to 440°C and a contact period of 5 to 7 seconds. From our calculations it is seen that the weight of propylene load per unit weight of catalyst per hour is about 0.050 WWH, with single pass yields of acrylonitrile at 82.0%. However there is no test data presented for acrylonitrile under conditions of high load rate and high pressure, and as such the performance of this catalyst under those conditions cannot be determined. Japanese patent JP7303836 introduces a Mo-Bi-Ce-Fe-Zn catalyst for acrylonitrile, with test conditions as follows: an internal diameter of 1 cm, pressure at 0.5 kg/cm², a temperature of 430°C with 60 g of catalyst in the reactor, in contact for a period of 6.0 seconds. According to our calculations, the weight of propylene load per unit weight of catalyst per hour is 0.042 WWH, with single pass yields of acrylonitrile at 80.0%. This patent does not present data for acrylonitrile under conditions of high load and high pressure either, and as such the performance of this catalyst under those conditions cannot be determined.

The goal of this invention is to make up for the lack of data in the abovementioned patents for the performance of acrylonitrile under conditions of high load and high pressure. This patent presents a new fluidized bed catalyst for propylene ammoxidation, such catalyst being suitable for use under conditions of high pressure and high propylene loads. It also is able to maintain high activity and high acrylonitrile single pass yield rates.

The technical proposal of this invention is as follows: A fluidized-bed catalyst for propylene ammoxidation, comprising silicon dioxide as support and a composite of the following formula:



A is at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, samarium;

B is one element selected from the group consisting of magnesium, zinc, cobalt, manganese, chromium, phosphorus, antimony, boron, tungsten, vanadium or a mixture thereof;

a, b, c, d, e, f, and i are ratios of A, B, sodium, lithium, strontium, iron, and nickel, respectively, to 12 molybdenum atoms, g is the ratio of a cerium atom to the sum of a bismuthum and a cerium atom, and h is the ratio between the sum of a bismuthum and a cerium atom to 12 molybdenum atoms; where

$$a = 0.001 \text{ to } 0.7;$$

$$b = 0.1 \text{ to } 10;$$

$c = 0.01$ to 0.7 ;

$d = 0.01$ to 0.7 , provided that a , c and d are 0.1 to 1.5 ;

$e = 0.01$ to 4 ;

$f = 0.5$ to 4 ;

$g = 0.3$ to 0.8 ;

$h = 0.5$ to 2 ;

$i = 0.5$ to 10 ;

x = number of oxygen atoms required to satisfy the valence requirement of the other elements present;

the content of silicon dioxide support in the catalyst is in the range of 30-70 percent by weight; wherein

a , c , and d are all in the preferred range of 0.2 to 1.0 ;

e , f , and i are in the preferred range of 0.01 to 2.5 , 1 to 3 and 2 to 8 respectively;

h is in the range of 0.7 to 2 ;

the content of silicon dioxide support in the catalyst is in the range of 40-60 percent by weight.

In this invention bismuth is partly replaced by cerium to increase catalyst yields and stability. The substitution of strongly-alkaline alkali earth metal strontium for an alkali metal, especially potassium or other alkali metals, further improves activity of the catalyst and decreases production of excessive carbon dioxide. The use of magnesium or zinc can make for a more reasonable distribution of post-catalytic reaction products, i.e. the amount of carbon monoxide and carbon dioxide produced is reduced. And the addition of lithium to the catalyst helps further to increase its activity, etc. The coordinated effect of each component endows the catalyst with a heightened performance. Operating under a reactive pressure of 0.14 MPa, a temperature of 440°C , a weight of propylene load per unit weight of catalyst per hour at 0.085 WWH, and reaching a maximum propylene conversion rate of 98.9% , it exhibits high catalytic activity. The single pass yield rate of acrylonitrile is still able to reach 79.7% , and it is suitable for use under conditions of high pressure and loads. This makes it very effective.

The catalyst of the present invention can be prepared by conventional methods; catalyst components, support, and water are first mixed to form a paste, followed by spray drying to form microspheres, and then calcining. The paste is prepared in accordance with the instructions in Chinese patent 87103455.7 (CN1005248B).

The raw materials selected for preparing the catalyst of the present invention are as follows:

Element A preferably originates from its nitrates, hydroxides, or salts which are decomposable to oxides.

The phosphorus, boron, tungsten and vanadium of Element B preferably originate from their corresponding acids or ammonium salts; antimony can originate from antimony trioxide, antimony pentoxide, antimony sol which can be hydrolyzed to antimony oxides; chromium preferably originates from chromium trioxide (the valence state of chromium is 6) chromium nitrate, or their mixture; the remaining can originate from their nitrates, hydroxides or oxides or salts which are decomposable to oxides. Salts used preferably originate from water soluble nitrates.

The sodium component can be selected from sodium nitrate, sodium hydroxide, sodium silicate, or any sodium compound which can be decomposable to oxide.

The lithium component can be selected from sodium nitrate, sodium hydroxide, sodium silicate, or any lithium compound which can be decomposable to oxide.

The components iron, nickel, bismuth, cerium and strontium can be selected from their oxides or their salts which are decomposable to oxides; salts used are preferably water-soluble nitrates.

The molybdenum component can be selected from molybdenum oxide or ammonium molybdate.

The catalyst was evaluated in a fluidized-bed reactor having an inner diameter of 38 mm. The amount of catalyst used was 400 g, the reaction temperature was 440°C, pressure was 0.14 MPa, mole ratio of propylene:ammonia:air = 1:1.2:9.8, and WWH was 0.085.

The definitions for the propylene conversion rate, acrylonitrile selectivity and single pass yield rates are as follows:

Propylene conversion rate (%) = $\frac{\text{reaction propylene mole number}}{\text{propylene load mole number}} \times 100$

Acrylonitrile selectivity (%) = $\frac{\text{produced acrylonitrile mole number}}{\text{reaction propylene mole number}} \times 100$

Acrylonitrile single pass yield rate (%) = $\frac{\text{produced acrylonitrile mole number}}{\text{propylene load mole number}} \times 100$

This invention is elaborated further by the following embodiments.

EMBODIMENT 1

Material A was prepared by dissolving a mixture of 1.8 g cesium nitrate, 3.22 g lithium nitrate, 2.4 g sodium nitrate and 5.9 g strontium nitrate in 30 g of water by heating.

Material B was prepared by dissolving 8.4 g chromium trioxide in 8.4 g of water.

Material C was prepared by dissolving 19.4 g ammonium tungstate in 100 ml of 5 percent by weight ammonia water, followed by mixing with a solution of 395.2 g ammonium molybdate in 325 g water of a temperature ranging from 50°C to 90°C.

Material D was prepared by dissolving a mixture of 40.7 g bismuth nitrate, 36.5 g cerium nitrate, 90.0 g magnesium nitrate, 282.1 g nickel nitrate and 135.7 g iron nitrate in 70 g water by heating.

Material A was mixed with 40 percent by weight silica sol 1250 g, to which materials B, C and D were added while stirring. After thoroughly stirring, a paste was formed, which was spray-dried according to conventional methods to obtain microspheres, followed by calcining at 610°C for 1 hour in a rotating oven with an inner-diameter of 89 mm and a length of 1700 mm ($\phi 89 \times 1700$ mm). The prepared catalyst had a composition as follows:

50% $\text{Cs}_{0.05} \text{Mg}_{1.9} \text{Cr}_{0.45} \text{W}_{0.45} \text{Na}_{0.15} \text{Li}_{0.23} \text{Sr}_{0.15} \text{Fe}_{1.8} \text{Bi}_{0.45} \text{Ce}_{0.45} \text{Ni}_{5.2} \text{Mo}_{12} \text{O}_x$ + 50% SiO_2 .

EMBODIMENTS 2 to 9 and COMPARATIVE EXAMPLES 1 to 3

The catalysts below, with their different components, were prepared basically by the process as described in Example 1, and acrylonitrile was produced by a propylene ammoxidation reaction under the following reactive conditions with said catalysts. Please see results at chart 1.

The reactive conditions for the examples and comparative examples are as follows:

ϕ 38 mm fluidized-bed reactor

temperature: 440 °C

pressure: 0.14 MPa

catalyst load: 400 g

WWH: 0.085/hr

material ratio (mole): $\text{C}_3 / \text{NH}_3 / \text{air} = 1/1.2/9.8$

[19] 中华人民共和国国家知识产权局

[51] Int. Cl⁷

B01J 23/755

B01J 23/888

[12] 发明专利申请公开说明书

[21] 申请号 99113805.8

[43] 公开日 2001 年 3 月 21 日

[11] 公开号 CN 1287882A

[22] 申请日 1999.6.24 [21] 申请号 99113805.8

[71] 申请人 中国石油化工集团公司

地址 100029 北京市朝阳区惠新东街甲 6 号

共同申请人 中国石油化工集团公司上海石油化工研
究院

[72] 发明人 安 炜 郭 平 戴毅敏 陈 欣

[74] 专利代理机构 上海石化专利事务所

代理人 袁明昌 郑存明

权利要求书 1 页 说明书 6 页 附图页数 0 页

[54] 发明名称 丙烯氨氧化流化床催化剂

[57] 摘要

本发明涉及一种丙烯氨氧化的流化床催化剂,含有
二氧化硅载体和化学式如下的 组合物: $A_xB_yNa_zLi_wSr_vFe_t$
 $(Bi_{1-x}Ce_x)_uNiMo_{12}O_{48}$, 式中 A 为选自钾、铷、铯、铊、钐
中的至少一种元素; B 为选自镁、锌、钴、锰、铬、磷、锑、
镉、钨、钼中的一种或多种元素。该催化剂具有能适应高
压、高负荷操作,同时具有高催化活性及高丙烯腈收率
的特点,可用于工业生产中。

ISSN 1008-4274

权利要求书

1、一种丙烯氨氧化流化床催化剂，含有二氧化硅载体和化学式如下的组合物：



式中 A 为选自钾、铷、铯、铊、钐中的至少一种元素；

B 为选自镁、锌、钴、锰、铬、锑、磷、硼、钨、钼中的一种或多种元素；

a、b、c、d、e、f、i 分别为 A、B、钠、锂、铈、铁、镍与 12 个钼原子之比，g 为铋原子与铋和铈原子之和之比，h 为铋和铈原子之和与 12 个钼原子之比；

其中：a 值为 0.001~0.7；

b 值为 0.1~10；

c 值为 0.01~0.7；

d 值为 0.01~0.7，条件是 a 值、c 值和 d 值之和为 0.1~1.5；

e 值为 0.01~4；

f 值为 0.5~4；

g 值为 0.3~0.8；

h 值为 0.5~2；

i 值为 0.5~10；

x 值为满足其它元素化合价所需氧原子数的总和；

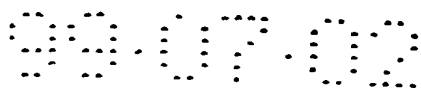
催化剂中载体二氧化硅含量以重量百分比计为 30~70%。

2、根据权利要求 1 所述丙烯氨氧化流化床催化剂，其特征在于 a 值、c 值和 d 值之和为 0.2~1.0。

3、根据权利要求 1 所述丙烯氨氧化流化床催化剂，其特征在于 e 值、f 值和 i 值分别为 0.01~2.5、1~3 和 2~8。

4、根据权利要求 1 所述丙烯氨氧化流化床流化床催化剂，其特征在于 h 值为 0.7~2。

5、根据权利要求 1 所述丙烯氨氧化流化床催化剂，其特征在于催化剂中载体二氧化硅含量以重量百分比计为 40~60%。



丙烯氨氧化流化床催化剂

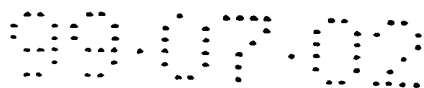
本发明涉及丙烯氨氧化流化床催化剂，尤其是关于含铈、铈和锂的丙烯氨氧化制丙烯腈流化床催化剂。

丙烯腈是重要的有机化工原料，它是通过丙烯氨氧化反应生产的。为获得高活性、高选择性的流化床催化剂，人们经过不断探索，进行了一系列改进。这些改进大都涉及催化剂活性部份，注重催化剂活性组份之间的搭配，来提高催化剂的活性与选择性，从而达到丙烯腈单程收率的提高，以及生产负荷的提高。

在丙烯腈生产装置中，希望丙烯腈催化剂能够在高丙烯负荷、高反应压力条件下使用，并达到高水平的反应性能，一直是丙烯腈工业生产中人们追求的目标。高负荷、高压反应条件可以提高丙烯腈产量和反应器的处理能力。耐高负荷催化剂对一定规模的生产装置而言，可减少催化剂装填量，并可使反应器扩能，这样工厂可以根据市场需求适当提高生产能力；耐高压催化剂可以满足日益提高的环保要求，吸收塔放空废气可依靠塔顶压力直接送入炉中燃烧，减少不经处理直接放空带来的空气污染。

高负荷、高压意味着反应气氛中反应物丙烯、氨和氧的浓度增加，它要求催化剂必须具备在单位时间内处理更多反应物的能力，因此丙烯腈催化剂在高负荷、高压条件下的反应性能，其实质是反映了催化剂活性和选择性的高低，对催化剂本身的综合性能提出了更高的要求。

文献 US4228098 中介绍了一种丙烯氨氧化生产丙烯腈工艺，其工艺中所用催化剂是以钼—铋—铁—钠—磷为主要活性组份，其催化剂组成中不含有铬元素，强调铋与铁在催化剂中保持一定的比例关系时，催化剂能发挥出较好的综合性能。该工艺中公开的催化剂考评条件为流化床反应器中催化剂丙烯负荷(WWH) 为 0.050 小时^{-1} 、反应压力为 0.05 MPa ，此时丙烯腈单收最高为 80.9% ，没有公开在高丙烯负荷、高反应压力条件下催化剂的考评数据，但从公开的数据中可以看出，在其它反应条件不变的情况下，反应压力 0.05 MPa 时的丙烯腈单收比常压下的考评数据低近 5% 。该文献存在以下缺点：一方面缺少高丙烯负荷、高反应压力条件下的数据，这样装置的生产能力较低；另一方面丙烯腈的单程收率也不高。文献 JP 平 7-289901 和 JP 平 7-328441 中分别介绍了一种 Mo-Bi-Ce-Fe-Co 体系的丙



烯腈流化床催化剂和 Mo-Bi-Ce-Fe-Ni 体系的丙烯腈流化床催化剂。该两份文献中规定了催化剂组成元素中铋与铈的对应关系，认为使用这种氨氧化催化剂组合物不仅能获得高产率的丙烯腈，而且即使在该生产过程延长反应时间也能有效地防止丙烯腈产率的降低。文献中公开的催化剂考评条件为流化床反应器中催化剂装填量 1000~2000 克、反应压力 0.5kg/cm²、反应温度 430~440℃、接触时间 5~7 秒，由计算可知催化剂丙烯负荷(WWH)为~0.050 小时⁻¹，此时丙烯腈单收最高为 82.0%，但它们均没有公开在高丙烯负荷、高反应压力条件下催化剂的考评数据，因此很难说明该催化剂在高压、高负荷条件下的操作性能。文献 JP 平 7-303836 中介绍了 Mo-Bi-Ce-Fe-Zn 体系的丙烯腈催化剂。该文献的催化剂考评条件为内径为 1 厘米，反应压力为 0.5kg/cm²，反应温度 430℃，反应器中催化剂装填量为 60 克，接触时间 6.0 秒，经计算丙烯负荷(WWH)为 0.042 小时⁻¹，此时丙烯腈单收最高为 80.0%。在该文献中同样没有涉及高压、高负荷操作条件的数据，因此也很难说明该催化剂在高压、高负荷条件下的操作性能。

本发明的目的是为了克服上述文献中催化剂不涉及高压、高负荷操作的缺点，提供一种新的丙烯氨氧化流化床催化剂，该催化剂适合于高反应压力、高丙烯负荷下操作，且同时能保持高的催化剂活性及丙烯腈单程收率。

本发明的目的是通过以下的技术方案来实现的：一种丙烯氨氧化流化床催化剂，含有二氧化硅载体和化学式如下的组合物：



式中：A 为选自钾、铷、铯、铊、钐中的至少一种元素；

B 为选自镁、锌、钴、锰、铬、锑、磷、硼、钨、钒中的一种或多种元素；

a、b、c、d、e、f、i 分别为 A、B、钠、锂、锶、铁、镍与 12 个钼原子之比，g 为铈原子与铋和铈原子之和之比，h 为铋和铈原子之和与 12 个钼原子之比；

其中：a 值为 0.001~0.7；

b 值为 0.1~10；

c 值为 0.01~0.7；

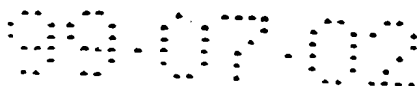
d 值为 0.01~0.7，条件是 a 值、c 值和 d 值之和为 0.1~1.5；

e 值为 0.01~4；

f 值为 0.5~4；

g 值为 0.3~0.8；

h 值为 0.5~2；



i 值为 0.5~10;

x 值为满足其它元素化合价所需氧原子数的总和;

催化剂中载体二氧化硅含量以重量百分比计为 30~70%。

上述技术方案中 a 值、c 值和 d 值之和的优选范围为 0.2~1.0; e 值、f 值和 i 值的优选范围分别为 0.01~2.5、1~3 和 2~8; h 值的优选范围为 0.7~2; 催化剂中载体二氧化硅含量以重量百分比计优选范围为 40~60%。

在本发明中用铈取代一部分铈可提高催化剂的产物收率和稳定性, 用强碱性的碱土金属锶取代一部分的碱金属, 尤其是钾或其它碱土金属, 一方面可进一步增强催化剂的活性, 同时有利于降低产生过多的二氧化碳, 使用镁或锌元素可使催化反应后, 目的产物的分布更趋合理, 即产物一氧化碳、二氧化碳的生成量有效降低, 催化剂中添加组份锂, 则有利于进一步提高催化剂的活性等。催化剂中各组份的协同作用, 赋予了催化剂较好的性能, 使催化剂在反应压力 0.14MPa, 反应温度 440℃, 丙烯负荷(WWH)为 0.085 小时⁻¹条件下操作, 其丙烯转化率最高可达 98.9%, 显示了很高的催化活性, 另外其目的产物丙烯腈的单程收率最高仍能达到 79.7%, 适合于高压、高负荷条件下操作, 取得了很好的效果。

本发明的催化剂制造方法可按常法进行。首先将催化剂各组份与载体和水混合成浆料, 经喷雾干燥成型为微球状, 最后焙烧制成催化剂。浆料的配制是将催化剂各组份的水溶液和载体按中国专利 87103455.7(CN1005248B)所述的方法进行。

本发明催化剂中各组份所使用的原料为:

组份 A 类元素最好用其硝酸盐、氢氧化物或可分解为氧化物的盐类。

组份 B 类元素中的磷、硼、钨、钼最好用其相应的酸类或其铵盐; 铈可用三氧化二铈、五氧化二铈、水解生成氧化铈的卤化物及铈溶胶; 组份铬最好用三氧化铬(六价铬)、硝酸铬或二者的混合物; 其它可用其硝酸盐、氢氧化物或氧化物或分解为氧化物的盐类, 所用的盐类最好是水溶性的硝酸盐。

组份钠可用硝酸钠、氢氧化钠、硅酸钠或任何可以分解的钠化合物。

组份锂可用硝酸锂、氢氧化锂、硅酸锂或任何可以分解的锂化合物。

组份铁、镍、铋、铈、锶可用其氧化物或分解为氧化物的盐类, 所用的盐类最好是水溶性的硝酸盐。

组份钼可用氧化钼或钼酸铵。

本发明催化剂的活性考评是在内径为 38 毫米的流化床反应器中进行的。催化剂装填量 400g, 反应温度 440℃, 反应压力 0.14MPa, 原料配比(摩尔)为丙烯: 氨: 空气=1: 1.2:

9.8, 催化剂的丙烯负荷(WWH)为 0.085 小时⁻¹。

在本发明中丙烯转化率、丙烯腈选择性和单程收率的定义如下:

$$\text{丙烯转化率 (\%)} = \frac{\text{反应的丙烯摩尔数}}{\text{丙烯进料摩尔数}} \times 100$$

$$\text{丙烯腈选择性 (\%)} = \frac{\text{生成丙烯腈摩尔数}}{\text{反应的丙烯摩尔数}} \times 100$$

$$\text{丙烯腈单程收率 (\%)} = \frac{\text{生成丙烯腈摩尔数}}{\text{丙烯进料摩尔数}} \times 100$$

下面通过实施例对本发明作进一步的阐述。

【实施例 1】

将 1.8 克硝酸铯、3.22 克硝酸锂、2.4 克硝酸钠和 5.9 克硝酸铟混合, 加水 30 克, 加热后溶解, 得物料(A); 将 8.4 克三氧化铬溶于 8.4 克水中, 得物料(B); 将 19.4 克钨酸铵溶于 100 毫升重量浓度为 5%的氨水中, 将 395.2 克钼酸铵溶于 325 克 50~90℃热水中, 将两溶液混合得物料(C); 将 40.7 克硝酸铋、36.5 克硝酸铈、90.9 克硝酸镁、282.1 克硝酸镍和 135.7 克硝酸铁混合, 加水 70 克, 加热后溶解, 得物料(D)。

将物料(A)与 1250 克重量浓度为 40%的硅溶胶混合, 在搅拌下加入物料(B)和 (C)和 (D), 充分搅拌得浆料, 按常法将制成的浆料在喷雾干燥器中成型为微球粒, 最后在内径为 89 毫米, 长度为 1700 毫米(Φ 89×1700mm)的旋转焙烧炉中于 610℃焙烧 1 小时, 制成的催化剂组成为: 50%Cs_{0.05}Mg_{1.9}Cr_{0.45}W_{0.45}Na_{0.15}Li_{0.25}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Ni_{5.2}Mo₁₂O₄+50%SiO₂

【实施例 2~9 及比较例 1~3】

采用与实施例 1 基本相同的方法制备具有下表中不同组成的催化剂, 并用所制得的催化剂在下面的反应条件下进行丙烯氨氧化生成丙烯腈的反应, 结果见表 1。

上述实施例与比较例的反应条件为:

Φ 38mm 流化床反应器

反应温度 440℃

反应压力 0.14MPa

催化剂装填量 400g

催化剂丙烯负荷(WWH) 0.085 小时⁻¹

99.07.02

原料配比(摩尔) $C_3/NH_3/空气 = 1/1.2/9.8$

表 1

实施例	催 化 剂 组 成	g	h	单 程 收 率 %			AN 选择 性, %	C ₃ 转化 率, %
				AN	CO	CO ₂		
实施例 1	50%Cs _{0.06} Mg _{1.9} Cr _{0.45} W _{0.45} Na _{0.15} Li _{0.25} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.2} Mo ₁₂ O ₄ +50%SiO ₂	0.50	0.90	79.7	4.3	7.1	80.7	98.6
实施例 2	50%K _{0.06} Mg _{1.9} Cr _{0.45} W _{0.45} Na _{0.15} Li _{0.25} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.2} Mo ₁₂ O ₄ +50%SiO ₂	0.50	0.90	78.9	4.2	6.7	80.0	98.6
实施例 3	50%Cs _{0.07} Mg _{2.1} Cr _{0.45} W _{0.45} Na _{0.15} Li _{0.09} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.0} Mo ₁₂ O ₄ +50%SiO ₂	0.67	1.35	79.1	4.3	7.5	80.0	98.8
实施例 4	50%Cs _{0.07} Mg _{2.1} Cr _{0.45} Mn _{0.45} Na _{0.15} Li _{0.09} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.0} Mo ₁₂ O ₄ +50%SiO ₂	0.67	1.35	78.9	4.1	6.5	79.8	98.9
实施例 5	50%Cs _{0.07} Zn _{2.1} Cr _{0.45} W _{0.45} Sb _{0.45} Na _{0.15} Li _{0.11} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.0} Mo ₁₂ O ₄ +50%SiO ₂	0.67	1.35	79.5	4.2	6.0	80.5	98.8
实施例 6	50%Cs _{0.07} Mg _{2.1} Cr _{0.45} P _{0.25} W _{0.25} Na _{0.15} Li _{0.11} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.0} Mo ₁₂ O ₄ +50%SiO ₂	0.67	0.75	79.0	3.9	7.0	80.3	98.4
实施例 7	50%Cs _{0.07} Zn _{2.1} Co _{2.0} Cr _{0.45} W _{0.45} Na _{0.15} Li _{0.15} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.0} Mo ₁₂ O ₄ +50%SiO ₂	0.59	1.10	79.3	4.3	6.7	80.5	98.5
实施例 8	50%Cs _{0.09} K _{0.03} V _{0.15} Mg _{2.0} Cr _{0.45} W _{0.45} Na _{0.15} Li _{0.17} Sr _{0.07} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.0} Mo ₁₂ O ₄ +50%SiO ₂	0.47	0.95	78.8	4.0	5.8	79.8	98.7
实施例 9	50%Cs _{0.09} Mg _{2.1} Cr _{0.45} Mn _{0.45} W _{0.25} Na _{0.15} Li _{0.15} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.2} Mo ₁₂ O ₄ +50%SiO ₂	0.59	1.10	78.9	4.0	7.1	80.0	98.6
比较例 1	50%Cs _{0.03} K _{0.13} Mg _{1.9} Cr _{0.45} W _{0.45} Na _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.2} Mo ₁₂ O ₄ +50%SiO ₂	0.50	0.90	77.3	3.5	8.7	79.3	97.5
比较例 2	50%Cs _{0.05} K _{0.05} Mg _{1.9} Cr _{0.45} W _{0.45} Na _{0.15} Sr _{0.15} Fe _{1.8} Bi _{0.45} Ni _{5.2} Mo ₁₂ O ₄ +50%SiO ₂	0	0.90	77.0	4.0	8.9	78.5	98.1
比较例 3	50%K _{0.2} Mg _{1.9} Cr _{0.45} W _{0.45} Na _{0.15} Fe _{1.8} Bi _{0.45} Ce _{0.45} Ni _{5.2} Mo ₁₂ O ₄ +50%SiO ₂	0.50	0.90	76.5	4.3	9.5	78.5	97.5